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Arsenic immobilization in anaerobic soils by the application of by-product iron materials obtained from the casting industry

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Abstract

Reducing the arsenic (As) concentration in rice grains is of great interest from a human health perspective. Iron (Fe) materials immobilize As in soils, thereby effectively reducing the As concentration in rice grains. We investigated the effect of by-product Fe materials obtained from the casting industry on the As mobility in two soils (soil A and soil B) by a long-term (approximately 100 days) flooded soil incubation experiment. The examined Fe materials were spent steel shot (SSS), fine spent casting sand containing steel shot (SCS), and two kinds of residual Fe materials from steel shot production (RIMs). Commercial Fe materials used to immobilize As (zero-valent Fe and ferrihydrite) were tested for comparison. The dissolved As in soil solution of controls for soil A and soil B reached approximately 100 and 800 μg L^{-1}, respectively. The effect on As immobilization of all the by-product Fe materials increased with time and was comparable to or greater than that of commercial ferrihydrite, except for SCS. The additions of SSS and RIMs decreased by more than 90% of the dissolved As in soil A and decreased by more than 50% in soil B after 100 days incubation. Overall, the effect of the by-product Fe materials on the solubility of silicon and phosphorus was much less than that of the commercial Fe materials. Considering the cost advantage over commercial Fe materials, the Fe materials obtained from the casting industry as by-products are promising amendments for the immobilization of As in paddy soils.

Key Words: Anaerobic soil, Arsenic immobilization, By-product iron, Phosphorus, Silicon

1. Introduction

Arsenic (As) species are hazardous chemicals that are ubiquitous in soils and plants. Since inorganic As species have greater toxicity than methylated species (Jain and Ali 2000), we need a strategy to decrease the concentration of inorganic As in foods. An important source of inorganic As for the Asian population is rice. For example, approximately 60% of the total intake of inorganic As by the average Japanese population was estimated to originate from rice (Oguri *et al*. 2014). In recent years, the Codex Alimentarius Commission adopted maximum permitted concentrations for inorganic As in polished and husked rice of 0.2 mg kg^{-1} and 0.35 mg kg^{-1}, respectively (Codex 2014; Codex 2016). Calculated from an investigation in Japan, approximately 2% of polished rice and 6% of brawn rice grains produced in 2012 contained inorganic As levels exceeding 0.20 mg kg^{-1} and 0.35 mg kg^{-1}, respectively (MAFF 2014). Therefore, agronomic management practices to attenuate the uptake of inorganic As in rice grains must be established.

Honma *et al*. (2016a) showed that the As concentration in rice grains was positively correlated with the dissolved As concentration in soils. Since rice plants absorb As from the soil solution, restricting As dissolution from soil to decrease As uptake by rice is an effective strategy. Rice cultivation under aerobic (i.e., oxidative, water-saving) conditions decreases the As load in rice grains (Xu *et al*. 2009) because the As dissolution from soils decreases under aerobic conditions. However, aerobic cultivation results in the undesired accumulation of another harmful element, cadmium (Cd), in rice grains (Arao *et al*.2009).

Another strategy for decreasing As dissolution from soils is the application of amendments to immobilize As in soils. Many studies reported that iron (Fe) materials such as Fe oxides (including hydroxides and oxyhydroxides) and zero-valent iron (ZVI) successfully immobilize As in soils (Kumpiene *et al*. 2008). Although most of the studies on As immobilization using amendments focused on polluted soils under aerobic conditions, some studies investigated the effect of Fe materials on As

mobility in non-polluted anaerobic soils, which are typical of Japanese paddy fields (Makino *et al*. 2016; Suda *et al*. 2016). Makino *et al*. (2016) showed that the combination of flooded cultivation and the application of Fe materials was an effective measure to keep both As and Cd in rice grains at low concentrations. Honma et al. (2016b) also demonstrated that commercially available converter furnace slag and Fe hydroxide decreased As and Cd uptake, respectively, by rice plants grown on paddy fields. However, the high cost of Fe materials would limit their agricultural use.

Less-expensive Fe materials can be supplied by the casting industry from the use and production of steel shot. After the use of the steel shot, large amounts of spent steel shot (SSS) and fine spent casting sand (SCS) collected with dust collectors are produced. Residual iron materials (RIMs), which contain substantial amounts of Fe materials, are formed in the process of steel shot production. These by-product Fe materials could be sold for agricultural use at low prices. Some reports showed that the application of steel shot was effective at immobilizing As in contaminated soils under aerobic conditions (Boisson *et al*. 1999; Mench *et al*. 2003).

Another concern regarding the agricultural use of Fe materials is the possible decrease in silicon (Si) and phosphorus (P) availability because both ZVI and Fe oxides remove these elements from solution (Jordan *et al*. 2007; Zhu *et al*. 2011; Su *et al*. 2001). These elements are useful or essential for the growth of rice plants and affect As uptake by rice because rice plants take up arsenite via the silicate transport pathway (Ma *et al*. 2008) and arsenate via phosphate-arsenate co-transporters (Meharg 2004). Therefore, how the application of Fe materials affects dissolved Si and P in anaerobic soils must be understood.

The objectives of the present study were to investigate (1) the effect of by-product Fe materials from the casting industry on As mobility during long-term soil incubation under anaerobic conditions, (2) the effect of Fe materials on solubility of P and Si in soils, and (3) to discuss the availability of these materials as practical amendments to immobilize As in anaerobic paddy fields.

2. Materials and methods

2.1 Soil samples

Soil samples were collected from the surface layer of a paddy field in 2013 (Soil A) and from the surface layer of a fallow paddy field in 2010 (Soil B_1) and in 2008 (Soil B_2). These soil samples were air-dried and then screened through 2-mm mesh sieves. Selected soil properties, including soil pH, total carbon and nitrogen content, clay content, content of selectively extractable (with dithionite-citrate, oxalate and pyrophosphate) elements, and hydrochloric acid-extractable As content, were measured as described by Suda *et al*. (2015). The data on the selected soil properties are listed in Table 1.

2.2 Fe materials

Fe materials from the casting industry were obtained from Sintokogio, Ltd. (Nagoya, Aichi, Japan). SSS is a mixture of spent steel shots collected from several foundries after use and then magnetically screened. SCS is composed of fine particles of spent casting sand with a small amount of steel shot. It is collected using dust collectors at foundries after sand removal in casting production. RIM-1 and RIM-2 are residual Fe materials of steel shot production. RIM-1 was obtained under wet conditions and was therefore dried at 30°C for several days. RIM-2 was collected using dust collectors at a steel shot production factory. Two types of commercial Fe materials, ZVI powder (cZVI) (Kobe Steel, Ltd., Tokyo, Japan) and ferrihydrite-based powder (cFH) (Ishihara Sangyo Kaisha, Ltd., Osaka, Japan) were used for comparison. Both cZVI and cFH are commercially supplied as amendments to immobilize As and heavy metals in soils. All the Fe materials were screened using 1-mm mesh sieves before use.

These Fe materials were digested with aqua-regia on a heating block, and the residue was

dissolved with hydrofluoric acid in a tightly sealed polypropylene tube at room temperature. Saturated boric acid was added to the tube to dissolve possible insoluble fluorides. The digested solution was used to quantify Fe, Si, Mn and P in the Fe materials. The Fe materials were also digested with an acid mixture (nitric acid:hydrochloric acid, 1:1) on a heating block to analyze the pseudo-total As in the Fe materials. The concentrations of elements in the digested solution were determined by inductively coupled plasma–optical emission spectrometry (ICP-OES; Vista-Pro, Agilent, California, USA) after dilution with ultra-pure water.

X-ray diffraction (XRD) analysis was carried out to clarify the mineral composition of the Fe materials. The Fe materials were passed through 212-μm mesh sieves after gentle grinding with an aluminum mortar if necessary and possible. Since most of the SSS particles were >212 μm and too hard to be crushed, both non-sieved (<1 mm) and sieved (<212 μm) fractions were analyzed by XRD. We adopted such a relatively large particle size to minimize the transformations of Fe minerals [e.g., Fe(II) oxidation] during long-term grinding. The Fe in SCS was condensed using a magnet because of the low Fe content of this material. XRD patterns were obtained under the following conditions: X-ray diffractometer, Rint2200 (Rigaku, Tokyo, Japan); Cu Kα, Ni filter; 40 kV, 40 mA; slit system, 1°–1°–0.15 mm. The scanned range was 20 to 85°2θ in 0.02° steps, with a scanning rate of 1° per min.

The particle-size distributions of the Fe materials were evaluated by sieving through mesh sizes of 0.850, 0.710, 0.600, 0.500, 0.425, 0.355, 0.300, 0.250, 0.212, 0.180, 0.150, 0.125, 0.106, 0.075, and 0.045 mm.

2.3. Anaerobic incubation of soil and quantification of elements in the soil solution

Soils A and B_1 were incubated under anaerobic conditions to clarify the effects of the Fe materials on the concentrations of As, Si and P in the soil solution. An air-dried soil sample (10 g, oven-dried basis) and 100 mg of each Fe material were mixed with 30 mL of ultra-pure water in a glass vial. A similar

157 sample without any Fe material was also prepared as a control. After nitrogen gas (N_2) bubbling for 2
158 min, the vial was capped with a butyl rubber cap and then tightly sealed with an aluminum cap. The
159 capped vial was shaken by hand and then incubated at 30 °C for approximately 20, 60 and 100 days.
160 The precise incubation periods were 21, 60, and 102 days for soil A and 20, 60, and 99 days for soil
161 B_1, respectively. The vial was shaken by hand with at 1-2-day intervals. These incubation experiments
162 were performed in triplicate.

163 After incubation, the soil solution was collected by a syringe connected to a needle (NN-2360C,
164 Terumo Corporation, Tokyo, Japan) with a 0.2-μm filter (DG2M-330, Spectrum Laboratories, Inc.,
165 CA, USA). The sampling unit was purged with N_2 before use. Approximately 4.5 mL of filtrate was
166 immediately mixed with 0.5 mL of 1.6 mol L^{-1} nitric acid to prevent Fe-hydroxide precipitation. The
167 acidified filtrate was diluted, and the Fe, Si, P and As concentrations in the diluted solution were
168 measured using ICP-OES and inductively coupled plasma–mass spectrometry (ICP–MS; Elan DRC-
169 e, PerkinElmer, Waltham, MA, USA).

170 The efficacy of the Fe materials in immobilizing As, Si and P in soils at each sampling time was
171 evaluated as the percent decrease in the dissolved elements compared with those in the control soils,
172 as defined by the following equation:

173 $$\text{Percent decrease in dissolved element} = \frac{(CE_{cont} - CE_{Fe})}{CE_{cont}} \times 100\ (\%) \quad (Eq.1)$$

174 where (CE_{Fe}) and (CE_{cont}) are the concentrations of the element in the soil solution incubated with and
175 without the Fe material, respectively.

176

177 ***2.4. Speciation of As in the soil solid phase***

178 Soil B_2 with or without cZVI was anaerobically incubated for 100 days in triplicate as described
179 in the former paragraph. The three incubated soil samples of each treatment were mixed under a N_2
180 atmosphere, and the mixture was then centrifuged to separate the soil solution from the solids. After

removing the soil solution, an aliquot of wet soil paste was packed into a polyethylene bag and kept frozen until analysis.

As K-edge (11867 eV) X-ray absorption near-edge structure (XANES) spectra were obtained on BL12C of the photon factory, KEK, and on BL5S1 of the Aichi Synchrotron Radiation Center. Reference materials, Na_2AsO_3 [As(III)], $NaHAsO_4$ [As(V)], orpiment (As_2S_3), and arsenopyrite (FeAsS, Francisco I. Madero Mine, Mexico, N's Mineral) were diluted by boron nitride, and the XANES spectra were collected in the transmission mode. The XANES spectra of the incubated soil pastes were collected in the fluorescence detection mode using a 19-element Ge semiconductor detector. The relative proportion of As species in the soil solid phases were calculated by linear combination fitting (LCF) of the XANES spectra with the reference materials. The fitting range was 11855 to 11885 eV. Athena in the Demeter 0.9.25 program package was used for XANES data analysis.

2.5. Statistical analysis

The dissolved element concentrations were subjected to two-way analysis of variance (ANOVA). Based on the output from ANOVA, multiple comparisons were made using Tukey's test at a 0.05 probability level. All statistical analyses were performed using Microsoft Excel and R software (version 3.1.1).

3. Results

3.1. Properties of Fe materials

Table 2 shows the concentrations of major elements and kinds of XRD-detectable minerals in the Fe materials. The concentrations of Fe and Si followed orders of cZVI > SSS >> RIM-2 > RIM-1 > cFH >>> SCS and SCS >>> RIM-1 = RIM-2 = SSS > cZVI = cFH, respectively. The As and P concentrations ranged from 3.27 to 76.8 mg kg^{-1} and from 102 to 639 mg kg^{-1}, respectively. The major

205 Fe minerals in each Fe material were Fe(0) for SSS, SCS and cZVI; wüstite and magnetite/maghemite
206 for RIM-1 and RIM-2; and ferrihydrite for cFH (Table 2, Fig. S1). Since steel shot-like spherical
207 particles were observed in the <212 mm fraction that accounted for approximately 12% of total weight,
208 the Fe(0) in RIM-2 (Fig. S1, f) should be derived from fine steel particles. All Fe materials were mainly
209 composed of Fe minerals except for SCS, which was dominated by quartz. Quartz in SSS and SCS
210 should originate from casting sand.
211 The particle distributions of the Fe materials are shown in Figure S2. RIM-1, cFH and cZVI
212 contained substantial amounts of particles in their finest fractions (less than 0.045 mm). The coarsest
213 Fe material was SSS. More than 30 wt% of the SSS particles did not pass through a 0.5 mm mesh
214 sieve.
215
216 ***3.2. Effect of Fe materials on As dissolution***
217 After soil incubation without Fe materials, the As concentrations in solution were 21.9 (day 20),
218 108 (day 60) and 98.2 (day 100) μg L^{-1} for soil A and 367, 649 and 817 μg L^{-1} for soil B_1, respectively
219 (Table 3). Two-way ANOVA demonstrated the significant effects ($P < 0.001$) of the Fe material, the
220 incubation time, and the interaction between the Fe material and incubation time on the dissolved As
221 concentration. Except for day 20 in soil A, the percent decrease in dissolved As in both soils decreased
222 in the following order at all incubation times: cZVI > SSS > RIM-2 = RIM-1 > SCS (Fig. 1). The
223 effect of these Fe materials on As immobilization increased over time, while that of cFH remained at
224 a similar level or gradually decreased.
225
226 ***3.3 As speciation in the soil solid phase with the addition of ZVI***
227 Figure 2 shows the As K-edge XANES spectra of soil B_2 incubated with and without cZVI under
228 anaerobic conditions. Without cZVI, the major As species in the soil solid phase was As(III), and the

229 percentages of As_2S_3-like species, As(III) and As(V) were 10, 72 and 18%, respectively. The XANES
230 spectra of soil incubated with cZVI had a distinct shoulder at approximately 11870 eV, which was not
231 apparent in the spectrum of the soil incubated without cZVI. This shoulder peak indicated the presence
232 of As associated with S. The percentages of FeAsS-like species, As_2S_3-like species, As(III) and As(V)
233 in the soil incubated with cZVI were 28, 15, 20 and 37%, respectively. Thus, the addition of cZVI
234 decreased the percentage of As(III) while increasing the percentages of As(V) and As associated with
235 S in the soil solid phase. Since we used synthesized or natural minerals as reference materials for As
236 associated with S in the LCF, the mineral crystallinity and exact elemental composition may be
237 different from those of As associated with S in the incubated soil. In addition, the LCF results represent
238 the presence of As species which have similar local coordinations with As_2S_3 and FeAsS, and not
239 necessary represent the presence of As_2S_3 and FeAsS exactly. Nonetheless, an increased contribution
240 of As species associated with S from the addition of cZVI was clearly observed in the XANES spectra.
241
242 ***3.4. Effect of Fe materials on the dissolved Si, P and Fe concentrations***
243 The concentration of Si dissolved from soils increased over time regardless of the addition of Fe
244 materials (Table 3). The Si concentrations were 8.02 (day 20), 11.3 (day 60) and 12.5 mg L^{-1} (day
245 100) in soil A and 11.1, 12.0, and 13.2 mg L^{-1} in soil B_1, respectively, without any Fe materials. Two-
246 way ANOVA revealed the significant effects of the Fe material, the incubation time, and the interaction
247 between the Fe material and incubation time on the dissolved Si ($P < 0.001$) (Table 3). The impact of
248 Fe materials on the dissolved Si concentration in soil A was slightly larger than that in soil B. For soil
249 A, the additions of SSS, SCS, and especially RIM-1 and RIM-2 caused significant increases in
250 dissolved Si (except for SSS at day 100). On the other hand, the applications of cFH and cZVI caused
251 statistically significant decreases in dissolved Si (Tukey test, $P = 0.05$) in all cases.
252 The dissolved P in soils increased with the incubation time (Table 3). The P dissolved from soils

253 without Fe materials was 1.15 (day 20), 2.01 (day 60) and 2.24 mg L^{-1} (day 100) in soil A and 0.480,
254 0.597, and 0.667 mg L^{-1} in soil B_1, respectively. Significant effects of the Fe material, the incubation
255 time, and their interaction on the dissolved P concentration were demonstrated by two-way ANOVA
256 ($P < 0.001$). The dissolved P significantly decreased due to the applications of cFH and cZVI, except
257 in soil A with cZVI at day 20. The additions of by-product Fe materials tended to decrease the
258 dissolved P in soil B_1, although the change was small and not statistically significant (Tukey test, $P =$
259 0.05) in most cases.
260 The concentration of Fe dissolved from soils without Fe materials increased over time, although
261 the change was not remarkable compared to the change in As (Table S1). The dissolved Fe content
262 was 49.8 (day 20), 97.6 (day 60) and 109 mg L^{-1} (day 100) in soil A and 85.0, 97.5, and 104 mg L^{-1}
263 in soil B_1, respectively (Table S1). The additions of Fe materials did not increase the dissolved Fe in
264 most cases. SSS and cZVI increased the dissolved Fe at day 20 in soil A, whereas cZVI (soil A and
265 B_1) and cFH (soil B_1) substantially decreased the dissolved Fe.
266
267 **4. Discussion**
268 ***4.1. As immobilization***
269 ***4.1.1. SSS, SCS and cZVI***
270 SSS and cZVI, which are composed mainly of ZVI, effectively decreased the As dissolution from soils
271 under the anaerobic conditions (Table 3, Fig. 1). The larger effect of cZVI on As immobilization
272 compared to that of SSS was probably attributable to the smaller particle size of cZVI (Fig. S2). SCS
273 decreased As dissolution less than SSS and cZVI did, reflecting the low content of Fe in SCS (Table
274 2). The percent decrease in dissolved As with the addition of these materials increased as time
275 proceeded (Fig. 1a and b). These results indicated that the Fe materials can immobilize As over a long
276 period even under anaerobic conditions.

277 Corrosion products of ZVI, mainly Fe oxides, are known to sorb As under aerobic conditions.
278 However, development of a corrosion layer of ZVI and the subsequent removal of As from solution is
279 limited under anaerobic conditions compared with aerobic conditions (Klas and Kirk 2013). Therefore,
280 the sorption of As onto the corrosion products of ZVI might not be a major mechanism restricting As
281 dissolution from soils under anaerobic conditions as in the present study.
282 The XANES spectra indicated that cZVI addition substantially increased the formation of As
283 species associated with S under anaerobic conditions (Fig. 2). Arsenopyrite was not observed in the
284 control soil but accounted for 28% of the total As in the soil incubated with cZVI. Therefore, As
285 precipitation as sulfides, especially as FeAsS-like species, might contribute to the As immobilization
286 caused by the application of cZVI, SSS and SCS. Hydrogen gas generation accompanying water
287 reduction by ZVI promotes microbial sulfate reduction (Gu *et al.* 1999) and possibly induces the
288 subsequent formation of insoluble sulfides of As and Fe.
289 The percentage of As(V) in the soil incubated with cZVI was substantially higher than that in the
290 control soil. Since the affinity of As(V) for soil solid phase is greater than that of As(III) (Takahashi *et*
291 *al*. 2003), As(III) oxidation is expected to decrease the As mobility in soils. Considering the strictly
292 anaerobic conditions of the incubation experiment, As(III) oxidation by dissolved oxygen and Fenton's
293 reaction unlikely occurred substantially. Instead, As(III) oxidation at the Fe oxide shell on ZVI surface
294 (Yan et al. 2010) might be an explanation. Yan et al. (2012) inferred that the As(III) oxidation by ZVI
295 caused via an Fe oxide-Fe(II)-As(III) ternary complex, which was an As(III) oxidation mechanism in
296 anaerobic Fe oxide-Fe(II) systems previously suggested by Amstaetter *et al.* (2010). Although we have
297 no evidence, the reaction should not be ruled out as a candidate mechanism for the As immobilization
298 in soils anaerobically incubated with cZVI, SSS and SCS.
299
300 ***4.1.2. RIM-1 and RIM-2***

The additions of RIM-1 and RIM-2 immobilized As in soils, although this immobilization was less effective than that by SSS and cZVI. Since these RIMs contained magnetite/maghemite and a small amount of hematite (only RIM-1), the sorption of As on these Fe oxides (Giménez *et al*. 2007) would contribute to As immobilization. However, As removal by wüstite, which is a major Fe mineral in these Fe materials, is limited under low-dissolved-oxygen conditions (Mishra and Farrell 2005). Interestingly, the percent decrease in dissolved As increased with time in both soils (Fig. 1). Although RIM-2 contained Fe(0), As immobilization by Fe(0) would be limited due to the small amount of Fe(0). Arsenic(III) was oxidized to As(V) at the surface of Fe oxides, including magnetite and hematite, even under anaerobic conditions (Yan *et al*. 2010). Since the oxidation is considered to occur via reactive Fe(III)-Fe(II) species and/or secondary Fe(II)/Fe(III) mineral phases (Amstaetter *et al*. 2010), it might be facilitated by increase of Fe(II) dissolution and secondary Fe precipitation as time proceeded. However, there is no experimental evidence to support this hypothesis. Further studies are needed to investigate Fe and As speciation in order to propose mechanisms for As immobilization under anaerobic soil conditions amended with Fe materials containing Fe(II) and Fe(II)/Fe(III) minerals.

4.1.3. cFH

The major component of cFH, ferrihydrite, has a large specific surface area (100-700 m^2 g^{-1}; Cornel and Schwertmann 2003) and therefore adsorbs large amounts of oxyanions such as arsenate and phosphate. The high specific surface area expected based on the small particle size (Fig. S2) might explain high efficiency of cFH in As immobilization. Unlike other Fe materials, the percent decrease in dissolved As remained at a similar level (Soil A) or gradually decreased (Soil B) over time. A similar trend was observed in a previous study (Suda *et al*. 2015) showing that As immobilization by synthetic ferrihydrite decreased with time under similar incubation conditions. Although the reductive transformation of ferrihydrite to magnetite temporary increases As retention (Kocar *et al*. 2006), prolonged anaerobic conditions cause As release that results from diminishing binding sites on the

surface of Fe oxides (Tufano and Fendorf 2008). Furthermore, As sorption onto Fe oxides would be inhibited by co-existing substances, such as silicate, phosphate, carbonate species, and dissolved organic matter (Jain and Loeppert 2000; Swedlund and Webster 1999; Brechbühl *et al*. 2012; Grafe *et al*. 2002). In the present study, the concentrations of carbonate and dissolved organic carbon were not measured, but Table S1 shows a decreasing trend in the dissolved Si/As and P/As ratios in the control soils as time proceeded. Therefore, the competition for adsorption sites on the cFH surface with co-existing dissolved silicate and phosphate would not be a major cause of the decrease in As immobilization efficiency with the addition of cFH.

4.2. Si and P dissolution

The impact of Fe materials on the dissolved Si concentration in soil A was greater than that on soil B. In soil A, the additions of RIM-1 and RIM-2 increased the dissolved Si most significantly, although the Si content in SCS was approximately six times greater than those in RIM-1 and RIM-2. This result reflects the difference in Si minerals among these Fe materials. RIM-1 and RIM-2 contain amorphous (i.e., not XRD-detectable) Si, whereas SCS contains quartz, which is hardly soluble in soil solution (Table 4). Since As(III) is transported by the same pathways as Si (Ma *et al*. 2008), dissolved Si inhibits the uptake of As by rice plants (Li *et al*. 2009). Therefore, RIM-1 and RIM-2 potentially decrease As uptake in rice plants by supplying dissolved Si. On the other hand, cFH resulted in the largest percent decrease in dissolved Si among all the Fe materials, which reached 24% in soil A and 18% in soil B_1, because of the Si sorption onto ferrihydrite (Swedlund and Webster 1999).

Figure 3 shows the relationships between the percent decrease in dissolved As and that in dissolved P in soil B_1 incubated with Fe materials. The regression line for the by-product Fe materials indicates that the percent decrease in dissolved P was positively correlated with that in dissolved As ($r = –0.723$, $P < 0.001$). This result indicated that As immobilization was accompanied by a decrease

in P solubility. However, the percent decrease in dissolved As was much greater than the percent decrease in dissolved P, except in the case of cFH. The considerable difference in the ratio of the percent decrease in dissolved As to that in dissolved P between cFH and the other Fe materials might reflect the presence of different mechanisms of As immobilization between these materials, i.e., the adsorption of As onto the surface hydroxyl groups of Fe oxides was not main mechanism of As immobilization by the Fe materials, other than cFH. The same analysis was not carried out for soil A because the percent decrease in dissolved As at day 60 and day 100 reached nearly 100% in most cases. Overall, the by-product Fe materials did not substantially decrease dissolved P in soil A as the commercial Fe materials did, except for SSS at day 100 (Table 3).

4.3. Potential of the by-product Fe materials to immobilize As in paddy soils

Due to their complex compositions, determining the precise mechanisms of As immobilization by the application of by-product Fe materials is difficult. However, the present study clearly showed the high ability of by-product Fe materials, namely SSS, RIM-1 and RIM-2, to immobilize As in flooded anaerobic soils. Although cZVI more effectively restricted As dissolution from soils, the application of by-product Fe materials is more cost-effective than the application of cZVI. Furthermore, the application of by-product Fe materials did not cause significant decreases in Si and P dissolution compared with cFH. (Table 3, Fig. 2). This is desirable for both plant growth and the inhibition of As uptake by these elements. Therefore, we concluded that these by-product Fe materials are promising amendments for As immobilization in paddy soils, at least on a single-use basis.

In most cases, the dissolved Fe in soils incubated with the Fe materials did not substantially increase (Table S1). This result indicated that the Fe materials were relatively stable under anaerobic conditions. However, we cannot rule out the possibility that excess the Fe(II) derived from Fe materials adsorbed onto the soil solid phase and/or precipitated as secondary Fe minerals such as siderite

(Yamaguchi *et al.* 2011). In either case, the applied Fe materials eventually dissolve as Fe(II), followed by reoxidization to Fe(III) by dissolved oxygen. Therefore, regardless of their mineral composition, the applied Fe materials will ultimately dissolve, but their effect will persist to some extent due to the increase in Fe oxides in the applied soils. The Fe materials applied to paddy soil are most likely altered after repeated cycles of anaerobic and aerobic conditions, but their resistance against dissolution in soil under paddy field conditions remains unclear. Long-term and field-scale experiments should be carried out to assess the time course of As mobility in soils with Fe materials before agricultural use.

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References

Amstaetter K, Borch T, Larese-Casanova P, Kappler A 2010: Redox transformation of arsenic by Fe(II)-activated goethite (α-FeOOH). Environ. Sci. Technol., 44, 102–108.

Arao T, Kawasaki A, Baba K, Mori S, Matsumoto S 2009: Effects of water management on cadmium and arsenic accumulation and dimethylarsinic acid concentrations in Japanese rice. Environ. Sci. Technol., 43, 9361–9367.

Boisson J, Mench M, Vangronsveld J, Ruttens A, Kopponen P, De Koe T 1999: Immobilization of trace metals and arsenic by different soil additives: Evaluation by means of chemical extractions. Commun. Soil Sci. Plant Anal., 30, 365–387.

Brechbühl Y, Christl I, Elzinga EJ, Kretzschmar R 2012: Competitive sorption of carbonate and arsenic to hematite: combined ATR-FTIR and batch experiments. J. Colloid Interface Sci., 377, 313–321.

Codex Alimentarius Commission. 2014: Thirty-Seventh Session CICG, Geneva; 2014 Jul 14–18. http://www.fao.org/fao-who-codexalimentarius/sh-proxy/en/?lnk=1&url=https%253A%252F%252Fworkspace.fao.org%252Fsites%252Fcodex%252FMeetings%252FCX-701-37%252FREP14_CACe.pdf (April, 2017)

Codex Alimentarius Commission. 2016: Thirty-Ninth Session CICG, Rome; 2016 27 June - 1 July. http://www.fao.org/fao-who-codexalimentarius/sh-proxy/en/?lnk=1&url=https%253A%252F%252Fworkspace.fao.org%252Fsites%252Fcodex%252FMeetings%252FCX-701-39%252FREPORT%252FREP16_CACe.pdf (April, 2017)

Cornell RM, Schwertmann U 2003: Surface area and Porosity. In: The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses, pp. 87–102. Wiley-VCH: Weinheim.

Giménez J, Martínez M, de Pablo J, Rovira M, Duro L 2007: Arsenic sorption onto natural hematite, magnetite, and goethite. J. Hazard. Mater., 141, 575–80.

Grafe M, Eick MJ, Grossl PR, Saunders AM 2002: Adsorption of arsenate and arsenite on ferrihydrite

421 in the presence and absence of dissolved organic carbon. J. Environ. Qual., 31, 1115–1123.
422 Gu B, Phelps TJ, Liang L, Dickey MJ, Roh Y, Kinsall BL, Palumbo AV, Jacobs GK 1999:
423 Biogeochemical dynamics in zero-valent iron columns: implication for permeable reactive barriers.
424 Environ. Sci. Technol., 33, 2170–2177.
425 Honma T, Ohba H, Kaneko A, Nakamura K, Makino T, Katou H 2016b: Effects of soil amendments
426 on arsenic and cadmium uptake by rice plants (Oryza sativa L. cv. Koshihikari) under different
427 water management practices. Soil Sci. Plant Nutr., 62, 349–356.
428 Honma T, Ohba H, Kaneko-Kadokura A, Makino T, Nakamura K, Katou H 2016a: Optimal Soil Eh,
429 pH, and Water Management for Simultaneously Minimizing Arsenic and Cadmium Concentrations
430 in Rice Grains. Environ. Sci. Technol., 50, 4178–4185.
431 Jain A, Loeppert R 2000: Effect of competing anions on the adsorption of arsenate and arsenite by
432 ferrihydrite. J. Environ. Qual., 29, 1422–1430.
433 Jain CK, Ali I 2000: Arsenic: Occurrence, toxicity and speciation techniques. Water Res., 34, 4304–
434 4312.
435 Jordan N, Marmier N, Lomenech C, Giffaut E, Ehrhardt JJ 2007: Sorption of silicates on goethite,
436 hematite, and magnetite: Experiments and modelling. J. Colloid Interface Sci., 312, 224–229.
437 Klas S, Kirk DW 2013: Advantages of low pH and limited oxygenation in arsenite removal from water
438 by zero-valent iron. J. Hazard. Mater., 252–253, 77–82.
439 Kocar BD, Herbel MJ, Tufano KJ, Fendorf S 2006: Contrasting effects of dissimilatory iron (III) and
440 arsenic (V) reduction on arsenic retention and transport. Environ. Sci. Technol., 40, 6715–6721.
441 Kumpiene J, Lagerkvist A, Maurice C 2008: Stabilization of As, Cr, Cu, Pb and Zn in soil using
442 amendments-a review. Waste Manag., 28, 215–225.
443 Li RY, Stroud JL, Ma JF, McGrath SP, Zhao FJ 2009: Mitigation of arsenic accumulation in rice with
444 water management and silicon fertilization. Environ. Sci. Technol., 43, 3778–3783.

445 Ma JF, Yamaji N, Mitani N, Xu X-Y, Su Y-H, McGrath SP, Zhao F-J 2008: Transporters of arsenite in
446 rice and their role in arsenic accumulation in rice grain. Proc. Natl. Acad. Sci. U. S. A., 105, 9931–
447 9935.
448 MAFF 2014: Survey of arsenic levels in brown rice and polished rice produced in Japan.
449 http://www.maff.go.jp/j/press/syouan/nouan/pdf/140221-01.pdf (in Japanese, October, 2015)
450 Makino T, Nakamura K, Katou H, *et al*. 2016: Simultaneous decrease of arsenic and cadmium in rice
451 (Oryza sativa L.) plants cultivated under submerged field conditions by the application of iron-
452 bearing materials. Soil Sci. Plant Nutr., 62, 340–348.
453 Meharg AA 2004: Arsenic in rice-understanding a new disaster for South-East Asia. Trends Plant Sci.,
454 9, 415–417.
455 Mench M, Bussière S, Boisson J, Castaing E, Vangronsveld J, Ruttens A, DeKoe T, Bleeker P,
456 Assunção A, Manceau A 2003: Progress in remediation and revegetation of the barren Jales gold
457 mine spoil after in situ treatments. Plant Soil, 249, 187–202.
458 Mishra D, Farrell J 2005: Evaluation of mixed valent iron oxides as reactive adsorbents for arsenic
459 removal. Environ. Sci. Technol., 39, 9689–9694.
460 Oguri T, Yoshinaga J, Tao H, Nakazato T 2014: Inorganic arsenic in the Japanese diet: Daily intake
461 and source. Arch. Environ. Contam. Toxicol., 66, 100–112.
462 Su C, Puls RW 2001: Arsenate and arsenite removal by zerovalent iron: Effects of phosphate, silicate,
463 carbonate, borate, sulfate, chromate, molybdate, and nitrate, relative to chloride. Environ. Sci.
464 Technol., 35, 4562–4568.
465 Suda A, Baba K, Akahane I, Makino T 2016: Use of water-treatment residue containing polysilicate-
466 iron to stabilize arsenic in flooded soils and attenuate arsenic uptake by rice (Oryza sativa L.) plants.
467 Soil Sci. Plant Nutr., 62, 111–116.
468 Suda A, Baba K, Yamaguchi N, Akahane I, Makino T 2015: The effects of soil amendments on arsenic

concentrations in soil solutions after long-term flooded incubation. Soil Sci. Plant Nutr., 61, 592–602.

Swedlund PJ, Webster JG 1999: Adsorption and polymerization of silicic acid on ferrihydrite, and its effect on arsenic adsorption. Water Res., 33, 3413–3422.

Takahashi Y, Ohtaku N, Mitsunobu S, Yuita K, Nomura M 2003: Determination of the As(III)/As(V) ratio in soil by X-ray absorption near-edge structure (XANES) and its application to the arsenic distribution between soil and water. Anal. Sci., 19, 891–896.

Tufano KJ, Fendorf S 2008: Confounding impacts of iron reduction on arsenic retention. Environ. Sci. Technol., 42, 4777–4783.

Xu XY, Mcgrath SP, Mehaarg AA, Zhao FJ 2009: Growing rice aerobically markedly decreases arsenic accumulation. Environ. Sci. Technol., 43, 5574–5579.

Yamaguchi N, Nakamura T, Dong D, Takahashi Y, Amachi S, Makino T 2011: Arsenic release from flooded paddy soils is influenced by speciation, Eh, pH, and iron dissolution. Chemosphere, 83, 925–932.

Yan W, Ramos MA V, Koel BE, Zhang WX 2010: Multi-tiered distribution of arsenic in iron nanoparticles: Observation of dual redox functionality enabled by a core shell structure. Chem. Commun., 46, 6995–6997.

Yan W, Ramos MA V, Koel BE, Zhang WX 2012: As(III) sequestration by iron nanoparticles: Study of solid-phase redox transformations with X-ray photoelectron spectroscopy. J. Phys. Chem. C, 116, 5303–5311.

Zhu J, Pigna M, Cozzolino V, Caporale AG, Violante A 2011: Sorption of arsenite and arsenate on ferrihydrite: Effect of organic and inorganic ligands. J. Hazard. Mater., 189, 564–571.

493 **Table and Figure Legends**

494

495 Fig. 1 Time course changes in the percent decrease in dissolved arsenic (As) in soil A (a) and soil B1
496 (b) incubated with each Fe material. SSS, SCS, RIM, cFH and cZVI denote spent steel shot, fine spent
497 casting sand, residual iron material of steel shot production, commercial ferrihydrite and commercial
498 zero-valent iron, respectively. The percent decrease in dissolved As was calculated using Eq. 1.

499

500 Fig. 2 Arsenic K-edge XANES spectra of solid phases of (a) the control for soil B2 and (b) soil B2
501 incubated with commercial zero-valent iron. Broken lines indicate the spectra of the reference
502 materials, Na_2AsO_3 [As(III)], $NaHAsO_4$ [As(V)], orpiment (As_2S_3) and arsenopyrite (FeAsS). Linear
503 combination fittings from the spectra of the reference materials for the soils are shown as solid lines.

504

505 Fig. 3 Relationship of the percent decrease in dissolved arsenic (As) and phosphorus (P) in soil B_1
506 incubated with the Fe materials. SSS, SCS, RIM, cFH and cZVI denote spent steel shot, fine spent
507 casting sand, residual iron materials of steel shot production, commercial ferrihydrite and commercial
508 zero-valent iron, respectively. The regression line is for the by-product Fe materials (SSS, SCS, RIM-
509 1 and RIM-2), and *** indicates significance at $P < 0.001$. The percent decrease in dissolved As and
510 P was calculated using Eq. 1.

511

512 Table 1 Selected physico-chemical properties of the soil samples

513

514 Table 2 Elemental and mineralogical composition of the iron materials

515

516 Table 3 Time course of the concentrations of arsenic (As), silica (Si) and phosphorus (P) in soil solution

517 and two-way analysis of variance (ANOVA)

Table 1 Selected physico-chemical properties of the soil samples

Soil sample	pH (H_2O)	TC ($g\ kg^{-1}$)	TN ($g\ kg^{-1}$)	Clay ($g\ kg^{-1}$)	Selective extraction ($g\ kg^{-1}$)				HCl-As ($mg\ kg^{-1}$)
					Fe_d	Al_o	Fe_o	Si_o	
Soil A	5.18	14.3	1.22	170	9.13	2.77	5.47	0.36	2.80
Soil B_1	6.54	16.3	1.58	349	19.1	1.60	10.5	0.70	5.83
Soil B_2†	5.99	17.7	1.74	359	17.8	1.59	10.1	0.52	8.36

TC, Total carbon; TN, Total nitrogen; HCl-As, arsenic extractable in 1 mol L^{-1} hydrochloric acid

Subscripts “o” and “d” denote oxalate- and dithionite-citrate-extractable elements, respectively.

† Data from Suda et al. (2015)

Table 2 Elemental and mineralogical composition of the iron materials

Fe material	Elemental concentration					Mineral	
	Fe (g kg^{-1})	Si (g kg^{-1})	Mn (g kg^{-1})	As (mg kg^{-1})	P (mg kg^{-1})	Major	Minor
SSS	864±43	50.2±15.2	6.22±0.09	37.5±4.1	592±4	Z	Q
SCS	56.4±13.0	355±1	1.48±0.11	3.27±0.47	102±1	Q	Z
RIM-1	590±13	59.8±1.6	50.5±0.9	3.77±0.86	380±14	W, M	H
RIM-2	642±18	57.4±2.2	49.3±1.9	19.5±4.4	406±16	W, M	Z
cFH	532±3	10.8±4.2	2.10±0.04	3.41±0.90	239±4	F	
cZVI	982±4	15.9±0.4	48.4±0.3	76.8±0.7	639±21	Z	

SSS, spent steel shot; SCS, fine spent casting sand; RIM, residual Fe materials of steel shot production; cFH, commercial ferrihydrite; cZVI, commercial zero-valent iron

Fe, iron; Si, silicon; Mn, manganese; As, arsenic; P, phosphorus

Z, zero-valent iron; Q, quartz; W, wüstite; M, magnetite and/or maghemite; H, hematite; F, ferrihydrite

Table 3 Time course of the concentrations of arsenic (As), silica (Si) and phosphorus (P) in soil solution and two-way analysis of variance (ANOVA)

Sample	Approximate incubation time (days)					
	Soil A			*Soil B* $_1$		
	20	60	100	20	60	100
Dissolved As (µg L $^{-1}$***)***						
Control	21.9±2.1 a	108±2 a	98.2±13.3 a	367±11 a	649±32 a	817±7 a
SSS	22.2±0.7 a	6.65±0.20 b	4.38±0.24 b	232±1 b	214±16 b	102±12 b
SCS	22.0±2.6 a	75.8±3.1 c	54.7±2.9 c	344±8 c	598±4 a	660±24 c
RIM-1	13.4±0.2 b	9.21±0.51 b	6.54±0.44 b	323±5 c	454±27 c	397±18 d
RIM-2	24.4±1.0 a	14.8±1.4 d	6.77±0.27 b	323±14 c	443±19 c	353±12 e
cFH	9.32±0.16 c	23.1±0.4 e	41.6±3.9 d	112±4 d	321±3 d	505±15 f
cZVI	2.67±0.36 d	1.57±0.02 f	2.53±0.35 b	72.9±5.7 e	11.1±0.9 e	5.36±0.17 g
Two-way ANOVA						
Fe material (F)		$P < 0.001$			$P < 0.001$	
Incubation time (T)		$P < 0.001$			$P < 0.001$	
$F \times T$		$P < 0.001$			$P < 0.001$	
Dissolved Si (mg L $^{-1}$***)***						
Control	8.02±0.10 a	11.3±0.1 a	12.5±0.1 a	11.1±0.2 a	12.0±0.1 ab	13.2±0.1 a
SSS	8.82±0.09 b	12.0±0.2 b	12.5±0.2 a	10.6±0.2 b	11.7±0.1 b	12.5±0.2 b
SCS	8.49±0.02 c	11.8±0.2 b	13.1±0.0 b	11.1±0.1 ab	12.1±0.0 a	13.4±0.1 a
RIM-1	10.8±0.1 d	13.3±0.1 c	14.1±0.1 c	11.2±0.2 a	12.1±0.3 a	13.4±0.1 a
RIM-2	10.1±0.1 e	13.0±0.0 c	13.7±0.0 d	10.9±0.0 ab	12.0±0.1 ab	13.3±0.2 a
cFH	6.07±0.07 f	9.06±0.10 d	11.8±0.3 e	9.11±0.02 c	10.6±0.2 c	12.0±0.1 c
cZVI	8.38±0.10 c	10.1±0.1 e	11.3±0.1 f	10.1±0.2 d	10.6±0.0 c	11.0±0.1 d
Two-way ANOVA						
Fe material (F)		$P < 0.001$			$P < 0.001$	
Incubation time (T)		$P < 0.001$			$P < 0.001$	
$F \times T$		$P < 0.001$			$P < 0.001$	
Dissolved P (mg L $^{-1}$***)***						
Control	1.15±0.03 a	2.01±0.01 ab	2.24±0.03 a	0.480±0.013 a	0.597±0.005 a	0.667±0.013 a
SSS	1.44±0.01 b	1.96±0.04 b	1.18±0.02 b	0.448±0.027 ab	0.579±0.034 a	0.561±0.016 b
SCS	1.17±0.02 a	2.02±0.02 ab	2.27±0.02 a	0.482±0.006 a	0.601±0.011 a	0.654±0.019 a
RIM-1	1.15±0.01 a	2.05±0.03 a	2.26±0.01 a	0.474±0.013 a	0.576±0.002 a	0.629±0.010 ac
RIM-2	1.20±0.02 c	1.99±0.02 ab	1.98±0.10 c	0.466±0.030 a	0.570±0.012 ab	0.604±0.017 c
cFH	0.435±0.01 d	1.03±0.02 c	1.27±0.14 b	0.259±0.000 c	0.359±0.012 c	0.459±0.012 d
cZVI	1.60±0.02 e	0.413±0.020 d	0.313±0.024 d	0.402±0.010 b	0.475±0.004 d	0.416±0.010 e
Two-way ANOVA						
Fe material (F)		$P < 0.001$			$P < 0.001$	
Incubation time (T)		$P < 0.001$			$P < 0.001$	
$F \times T$		$P < 0.001$			$P < 0.001$	

SSS, spent steel shot; SCS, fine spent casting sand; RIM, residual iron material of steel shot production; cFH, commercial ferrihydrite; cZVI, commercial zero-valent iron. Values followed by the same letter within a column are not significant ($P = 0.05$, Tukey's test).

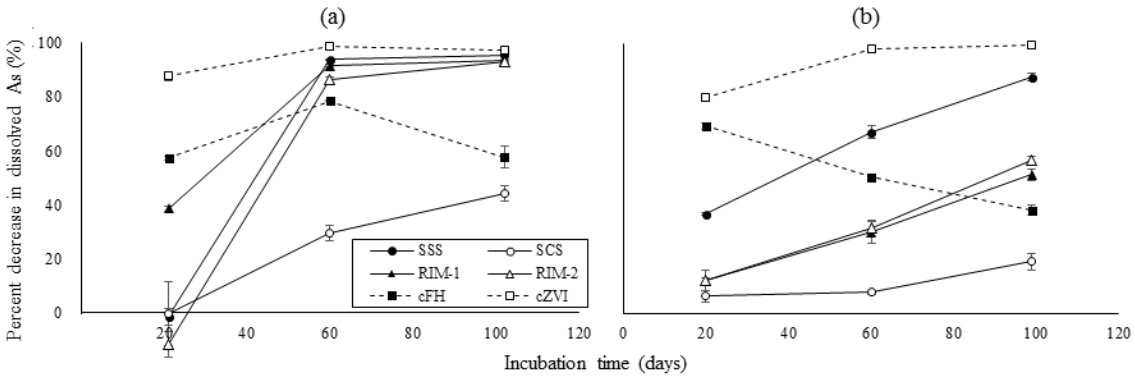

Fig. 1 Time course changes in the percent decrease in dissolved arsenic (As) in soil A (a) and soil B1 (b) incubated with each Fe material. SSS, SCS, RIM, cFH and cZVI denote spent steel shot, fine spent casting sand, residual iron material of steel shot production, commercial ferrihydrite and commercial zero-valent iron, respectively. The percent decrease in dissolved As was calculated using Eq. 1.

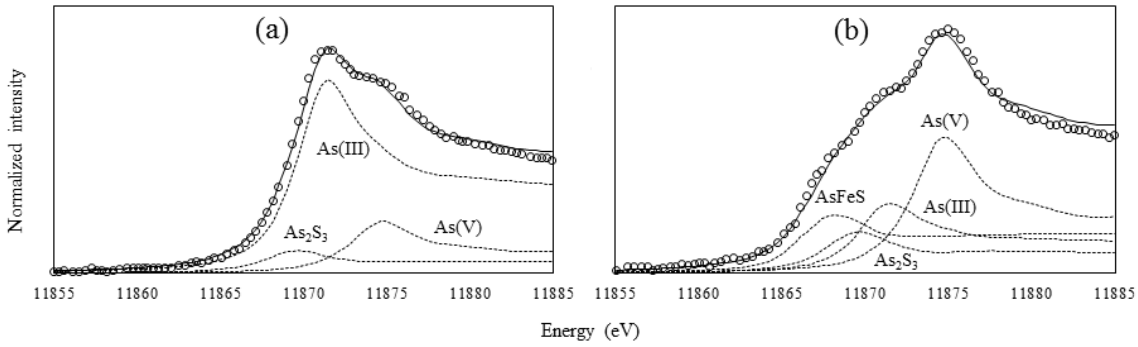

Fig. 2 Arsenic K-edge XANES spectra of solid phases of (a) the control for soil B2 and (b) soil B2 incubated with commercial zero-valent iron. Broken lines indicate the spectra of the reference materials, Na_2AsO_3 [As(III)], $NaHAsO_4$ [As(V)], orpiment (As_2S_3) and arsenopyrite (FeAsS). Linear combination fittings from the spectra of the reference materials for the soils are shown as solid lines.

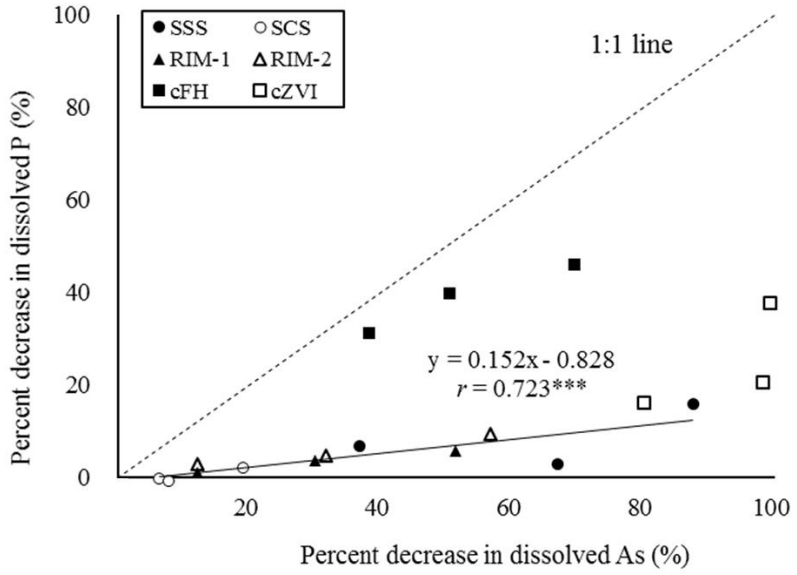

Fig. 3 Relationship of the percent decrease in dissolved arsenic (As) and phosphorus (P) in soil B_1 incubated with the Fe materials. SSS, SCS, RIM, cFH and cZVI denote spent steel shot, fine spent casting sand, residual iron materials of steel shot production, commercial ferrihydrite and commercial zero-valent iron, respectively. The regression line is for the by-product Fe materials (SSS, SCS, RIM-1 and RIM-2), and *** indicates significance at $P < 0.001$. The percent decrease in dissolved As and P was calculated using Eq. 1.